

PATENT ABSTRACTS OF JAPAN

(11)Publication number : **11-224670**

(43)Date of publication of application : **17.08.1999**

(51)Int.Cl.

H01M 4/62

H01M 2/34

H01M 4/02

H01M 10/40

(21)Application number : **10-022965**

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(22)Date of filing : **04.02.1998**

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(54) LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To increase safety at the time of a temperature rise due to overcharging without decreasing the active material fill of a positive electrode and a negative electrode by providing a current interrupting means operated as the battery internal pressure rises, and forming the positive electrode with a positive electrode active material mainly made of a transition metal oxide, a conductive auxiliary containing a carbon material adsorbing the gas desorbable by heat, and a binder.

SOLUTION: A carbon material adsorbing the gas desorbable by heat and having a large specific surface area is used as the conductive auxiliary of a positive electrode. When the internal pressure is increased by the gas generated at the time of a temperature rise due to overcharging, a current is interrupted by a pressure valve, and explosion is prevented.

The specific surface area of the carbon material is preferably set to 50-5000 m²/g. The conductive auxiliary preferably contains one or more of a graphite material adsorbing the gas of CO₂, CO, N₂ or Ar, granular activated carbon with the grain size of 150 μm or above, powdery activated carbon with the grain size below 150 μm, carbon black, an amorphous carbon material, and cellulose fibered activated carbon.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

CLAIMS

[Claim(s)]

[Claim 1] It is the lithium secondary battery which a current cutoff means to operate according to lifting of cell internal pressure in a positive electrode, a negative electrode, and the rechargeable battery using the lithium ion insertion elimination reaction which has nonaqueous electrolyte is provided, and this positive electrode consists of positive active material which makes a transition-metals oxide a subject, an electric conduction assistant containing a carbon material, and a binder, and this electric conduction assistant is what adsorbed gas, and is characterized by to be the carbon material in which a gas evolution is possible with heat.

[Claim 2] The positive active material with which a current cutoff means to operate according to lifting of cell internal pressure in a positive electrode, a negative electrode, and the rechargeable battery using the lithium ion insertion elimination reaction which has nonaqueous electrolyte is provided, and this positive electrode makes a transition-metals oxide a subject, It is the lithium secondary battery which specific surface area consists of an electric conduction assistant in which the carbon material which are below 5000m² / g is included more than 50m² / g, and a binder, and this electric conduction assistant is what adsorbed gas, and is characterized by being the carbon material in which a gas evolution is possible with temperature.

[Claim 3] the granular active carbon which is the graphite ingredient into which a conductive auxiliary adsorbs the gas of CO₂, CO, N₂, and Ar, and is desorbed from gas with heating, and the particle size of 150 micrometers or more, the powdered activated carbon which is the particle size of less than 150 micrometers, carbon black, and an amorphous carbon ingredient -- or Claim 1 characterized by being constituted including at least one of cellulose system fibrous activated carbon, acrylic nitril system fibrous activated carbon, phenol system fibrous activated carbon, pitch system fibrous activated carbon, and the PAN system fibrous activated carbon, or a lithium secondary battery given in dyadic.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention relates to the nonaqueous electrolyte lithium secondary battery of the sealing structure of an explosion-proof type about the lithium secondary battery of nonaqueous electrolyte.

[0002]

[Description of the Prior Art] In recent years, computerization of the Internet etc. progresses and small lightweight-ization of portable electronic terminals, such as a cellular phone and a portable note type personal computer, which is migration communication equipment is progressing quickly. Moreover, small [of portable AV equipments, such as a digital camera, and a 8mm video camera, a magnetic-disk player] and lightweight-ization are also progressing.

[0003] Conventionally, as a rechargeable battery used for these electronic equipment, although the nickel hydride battery and the nickel-cadmium battery were known, since the weight of a cell was heavy, these had the fault that the energy density per weight was small, and suited the inclination for a device to become heavy, low [cell voltage]. Because of the formation of small lightweight, cell voltage is high, and it is required that a lithium secondary battery with the high energy density per weight should be adopted, and lightweight-ization of a device should be attained.

[0004] By the way, generally, with the nonaqueous electrolyte lithium secondary battery of closed mold, when the current more than predetermined quantity of electricity flows at the time of charge and failure of a battery charger and a cell activity device is benefited into a overcharge condition, a cell becomes an elevated temperature, the chemical reaction inside a cell is accelerated, and there is risk of explosion and ignition. Then, a positive electrode is LiCoO_2 . In the rechargeable battery using the nonaqueous electrolyte to which it considered as the subject and the negative electrode made the carbon material the subject, when a bigger current than a convention current flows, the protection network which intercepts a current is prepared or the protection component of a cell is prepared. Moreover, it has the current cutoff device which operates according to lifting of internal pressure for explosion prevention, and the cleavage valve which operates by a certain pressure.

[0005] In order to raise the safety of these cells, the technique which adds Li_2CO_3 inside a nonaqueous rechargeable battery is indicated by JP,1-286263,A and JP,4-329268,A. It prevents these disassembling electrochemically the lithium carbonate added to the positive electrode, when Li_2CO_3 is added to a positive electrode in the nonaqueous electrolyte rechargeable battery equipped with the relief valve and the potential of a positive electrode becomes high at the time of overcharge of a cell, and making cell internal pressure high by emitting carbon dioxide gas, operating a relief valve, and a cell overcharging them.

[0006]

[Problem(s) to be Solved by the Invention] However, even if it provided the structure of the above-mentioned explosion-proof type sealing cell, when it changed into a overcharge condition, the cell might be damaged, without the ability suspending the

anomalous reaction inside a cell -- the timing to which a current interrupting device operates is not fixed, and temperature rises quickly -- at an early stage.

[0007] Moreover, when adding Li_2CO_3 and Na_2CO_3 , there are many 1 - 10% and the additions of 0.5 - 15% of the weight of positive-electrode weight and negative-electrode weight, and the fill into the cell of an active material decreases and it is disadvantageous to high-capacity-izing of a cell. So, in this invention, before not decreasing the quantity of the active material fill of a positive electrode and a negative electrode and exploding and destroying a cell by fire by the thermal-run-away reaction accompanying the temperature rise in the cell at the time of overcharge of a cell, it aims at offering a cell with high safety by the high capacity which releases a relief valve, performs current cutoff and prevents explosion destruction by fire.

[0008]

[Means for Solving the Problem] Above-mentioned The means for solving a technical problem has the following descriptions. In the cell equipped with a current cutoff means to by_ which this invention operates according to lifting of cell internal pressure with a positive electrode, a negative electrode, and the rechargeable battery using the lithium ion insertion elimination reaction which has nonaqueous electrolyte, it is characterized by for this positive electrode to consist of positive active material which makes a transition-metals oxide a subject, an electric conduction assistant containing a carbon material, and a binder, and for specific surface area to be below $5000\text{m}^2/\text{g}$ more than $50\text{m}^2/\text{g}$, and to constitute this carbon material.

[0009] If specific surface area computes the volume of the gas by which the carbon material of $5000\text{m}^2/\text{g}$ is adsorbed more than $50\text{m}^2/\text{g}$ and 1g or more of amounts which serve as a value of about 12 to about 1150 ml/g, and are used in the cell exists When an outside dimension uses a cell can with a diameter [of 18mm], and a die length of 65mm also as 30%, cell internal pressure will take place [internal pressure lifting beyond 1.0 atmospheric-pressure -40 atmospheric pressure] the amount of desorption by the temperature rise.

[0010] For example, when specific surface area used 1g of carbon materials of $50\text{m}^2/\text{g}$ and an outside dimension uses a cell can with a diameter [of 18mm], and a die length of 65mm, if adsorption gas carries out degasifying 20% and cell internal pressure will carry out degasifying 100% 0.7 atmospheric pressures, internal pressure lifting of 3.3 or more atmospheric pressures will take place. By this internal pressure lifting, a pressure valve is operated promptly and the safety of a cell is raised.

[0011] Thus, by generation of heat, by using carbon material with a large specific surface area [finishing / the gas adsorption in which degasifying is possible] for the electric conduction assistant of a positive electrode, gas is generated in connection with the temperature rise at the time of the abnormalities of cells, such as overcharge, internal pressure is raised, a current is intercepted by actuation of a pressure valve, and explosion is prevented.

[0012]

[Embodiment of the Invention] The gestalt of operation of this invention is explained below.

[0013] First, the description of the lithium secondary battery by this invention as a conclusion of the knowledge which these artificers acquired is described, and the outline of the gestalt of operation is explained. In addition, about a concrete example, it mentions

later.

[0014] The lithium secondary battery by this invention for attaining the above-mentioned object consists of a positive electrode, a negative electrode, and the organic electrolytic solution, and in the rechargeable battery using a lithium ion insertion elimination reaction, its specific surface area is large and it makes carbon with the large amount of gas adsorption the electric conduction assistant of a positive electrode or a negative electrode after gas adsorption processing.

[0015] Although it is realizable as positive active material no matter what active materials [a transition-metals oxide, a transition-metals sulfide, the organic compound of the poly aniline system, and / other] it may use, preferably especially LiCoO_2 , $\text{LiXNi}_{1-y}\text{MyO}_2$, $\text{LiXM}_{1-y}\text{Co}_y\text{O}_2$, and $\text{Li}_x\text{Mn}_{1-y}\text{MyO}_2$ ($0 < x \leq 1.3$, $0 \leq y \leq 1$, $0 \leq z < 2$, M:aluminum, and Fe, Cu, Co, Mg, calcium, V, nickel, Ag and Sn --) Among the second transition-metals elements, at least one or more sorts, the ** lithium manganic acid ghost of LiMn_2O_4 and $\text{Li}_4\text{Mn}_5\text{O}_{12}$ grade, or $\text{Li}_x\text{Mn}_{2-y}\text{MyO}_{4-z}$ ($0 < x \leq 1.3$, $0 \leq y < 2$, $0 \leq z < 2$, M:aluminum, and Fe, Cu, Co, Mg, calcium, V, nickel, Ag and Sn --) It is the ** lithium oxide shown with at least one or more sorts of chemical formulas of the second transition-metals element.

[0016] On the other hand as a negative-electrode active material, a metal lithium, a lithium alloy For example, (LiAl , LiPb , LiSn , LiBi , LiCd), etc., The conductive polymer which doped the lithium ion (for example, polyacetylene, polypyrrole, etc.), What contained the lithium among the layers (for example, TiS_2 , MoS_2 , etc.) of the intercalation compound which mixed the lithium ion during the crystal, Or the carbonaceous ingredient in which a dope and a dedope of a lithium are possible, an intermetallic compound like silicide, a metallic oxide, or all the ingredients that emit [occlusion and] a lithium are usable.

[0017] Moreover, the aprotic organic electrolytic solution made to dissolve this electrolyte in an organic solvent is used for the electrolytic solution by using lithium salt as an electrolyte. As an organic solvent, ester, ether, 3 permutation-2-oxazolidinone, two or more sorts of these partially aromatic solvents, etc. are used here. If it illustrates concretely, as ester, they will be chain-like dimethyl carbonate, such as alkylene carbonate (ethylene carbonate, propylene carbonate, gamma-butyrolactone, 2-methyl-gamma-butyrolactone, etc.), diethyl carbonate, ethyl methyl carbonate, etc. As ether, a tetrahydrofuran and its substitution product, dioxolane, etc. are 1, 4-dioxolane, a pyran, a dihydropyran, tetrahydropyran, etc. as the ether which has six membered-rings as diethylether, dimethoxyethane, diethoxy ethane, and cyclic ether, for example, the ether which has five membered-rings. As an electrolyte, it is lithium perchlorate, hoe lithium fluoride, a chlorination ulmin acid lithium, lithium halide, a trifluoro methansulfonic acid lithium, and LiPF_6 , LiAsF_6 and $\text{LiB}(\text{C}_6\text{H}_5)_4$. It is usable and a 6 fluoride [phosphoric acid] lithium, hoe lithium fluoride, and lithium perchlorate are desirable especially. However, it is not limited to the above-mentioned instantiation with all the organic usable electrolytic solutions that used lithium salt as the supporting electrolyte. The carbon materials of the high specific surface area used by this invention are the graphite ingredient which has the high specific surface area 50m^2 / more than g, and can be desorbed from the gas of CO_2 , CO , N_2 , Ar , and others with heating, granular active carbon, the powdered active carbon which is the particle size of 150 micrometers or more, the fibrous activated carbon which is the particle size of less than 150 micrometers,

carbon black, an amorphous carbon ingredient, etc., and there is no constraint in the class and process hysteresis. It is a cellulose system, an acrylic nitril system, a phenol system, a pitch system, and a PAN system, and specific surface area is $1000\text{m}^2/\text{g}$ - $5000\text{m}^2/\text{g}$, and fibrous activated carbon has many amounts of desorption, and since the rate is also quick, it is suitable. Moreover, the carbon material with which degasifying is promoted above at least 60 degrees C is more desirable.

[0018] The structure of the cell produced in each example and the example of a comparison which are mentioned later is shown in drawing 1. The nonaqueous electrolyte rechargeable battery concerning this invention winds the positive electrode 2 which comes to apply positive active material to the positive-electrode charge collector 1 like drawing 1, and the negative electrode 4 which comes to apply a negative-electrode active material to the negative-electrode charge collector 3 through a separator 5, and where [of this winding object] an insulator 6 is ****(ed) up and down, it contains it with the cell can 7.

[0019] said cell can 7 -- the cell lid 8 -- a gasket 9 -- minding -- by closing, it is attached and the positive electrode, negative electrode, and terminal 10 of a cell are connected electrically, respectively. As for the positive-electrode terminal, connection with a cell lid is achieved through the component 11 for current cutoff. By deforming with internal pressure, the component for current cutoff intercepts a current and has composition which prevents explosion.

[0020] (Example 1) The carbon material used as an electric conduction assistant of a positive electrode was adjusted as follows. Specific surface area cooled the artificial graphite with a mean particle diameter of 1 micrometer after 1-hour heating at 300 degrees C among the vacuum by $280\text{m}^2/\text{g}$, and made Ar gas adsorb. The positive electrode was produced as follows. After mixing PVDF (polyvinylidene fluoride) (4.3 % of the weight) of the binder which the cobalt acid lithium (87 % of the weight) of about 15 micrometers of mean diameters which are an artificial graphite (8.7 % of the weight) and positive active material was made to dissolve in an electric conduction assistant at a N-methyl-2-pyrrolidone (for it to outline Following NMP) and making it the shape of a paste, double spread was carried out to aluminum foil with a thickness of 20 micrometers, and it dried at 80 degrees C for 2 hours. [finishing / this Ar adsorption] Pressing was carried out after that, and it heat-treated at 120 degrees C among the vacuum for 2 hours, and cooled in inert gas, and the positive electrode was obtained. Then, in order to compensate the part which carried out degasifying by electrode desiccation, it is Ar gas at the temperature of 20 degrees C or less 1.2 Re-adsorption treatment was performed with the atmospheric pressure. The electrode which performed gas adsorption was stored in the bottom of 20 degrees C and the re-adsorption gas ambient atmosphere of one or more atmospheric pressures till winding.

[0021] The negative electrode was produced by the approach shown below. To the artificial graphite, the double spread of what was mixed so that PVDF might become to a carbon material at 10% of the weight, and made the PVDF solution the shape of a paste [NMP] was carried out to the charge collector of copper foil with a thickness of 20 micrometers as a binder, and 3h dried at 80 degrees C. After carrying out rolling shaping by the roll press after that, 2h dried at 120 degrees C among the vacuum.

[0022] And the lead made from nickel was wound around the product made from aluminum, and the negative electrode at the curled form at the positive electrode through

installation and the porous membrane separator made from polyethylene with a thickness of 25 micrometers, respectively, and it contained with the cell can whose outside dimension is diameter 18mmx65mm. The center pin 12 was inserted after winding. Then, using 1 M-LiPF₆ / EC+DMC (1:1) as the electrolytic solution, after pouring this in, it obturated, and it considered as the cell A of this invention.

[0023] (Example 2) Ar gas adsorption processed the fibrous activated carbon of specific surface area of 2500m² / g of a phenol system to the electric conduction assistant of a positive electrode, Ar gas was made to re-stick to an electrode further, and also the cell was produced like the example 1, and it considered as the cell B of this invention.

[0024] (Example 3) To the electric conduction assistant of a positive electrode, it is CO₂ about the fibrous activated carbon of specific surface area of 1000m² / g of a PAN system. Gas adsorption processing is carried out and it is CO₂ further to an electrode. Gas was made to re-adsorb, and also the cell was produced like the example 1, and it considered as the cell C of this invention.

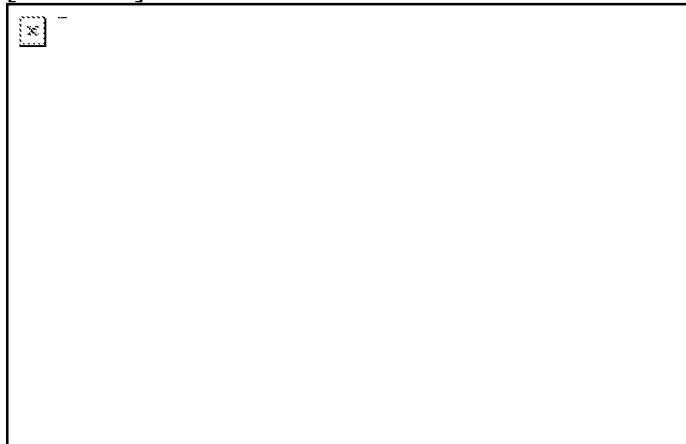
[0025] (Example 4) It is activated carbon of specific surface area of 3950m² / g which used MCMB as the raw material at the electric conduction assistant of a positive electrode N₂ It is used after gas adsorption processing and is N₂ further to an electrode. Gas was made to re-adsorb, and also the cell was produced like the example 1, and it considered as the cell D of this invention.

[0026] (Example of a comparison) Specific surface area used the artificial graphite with a mean particle diameter of 8 micrometers for the electric conduction assistant of a positive electrode by 10m² / g, and also the cell was produced like the example 1, and it considered as the comparison cell.

[0027] It produces 15 above-mentioned cells at a time respectively, and the result of having investigated the incidence rate of the cell by which the ignition when charging to 100% of rated capacity with Currents 2.5A and 4.0A and a burst produced these cells is shown in a table 1.

[0028]

[A table 1]



[0029] it is shown in a table 1 -- as -- charging current 2.5A **** -- breakage was seen by only the comparison cell which is not using the carbon material with which specific surface area carried out gas adsorption greatly. Moreover, the cell which applied this invention is 4.0A. It became clear that safety is improving to the example of a

comparison even when it overcharges, and especially the thing of safety with which specific surface area filled up the large carbon material improved. In addition, in order not to decrease the amount of active materials of an electrode, the effect to the energy density of a cell is small, and effectiveness of enough is in high capacity-ization of a cell.

[0030] Although applied to a cylindrical cell, this example is applicable, if it is not concerned with the size of a cell, and a configuration, for example, the component for current cutoff by internal pressure sensing is provided also in the cell of a square shape.

[0031] Moreover, although the thing of a configuration of intercepting a current and preventing explosion, when the component for current cutoff deforms with internal pressure was used in this example, the structure of releasing internal pressure intercepts a current with cell internal pressure by having attached further, if this current cutoff component is an insurance component which prevents explosion, it can apply it with any structure, and there is instead of [no] in that effectiveness being remarkable.

[0032]

[Effect of the Invention] According to this invention, specific surface area is large as above-mentioned, and by using the carbon material which carried out gas adsorption for the electric conduction assistant of a positive electrode, a pressure switch can operate because degasifying of the adsorption gas is carried out to abnormality generation of heat of a cell and the internal pressure of a cell rises rapidly, and explosion and destruction by fire can be prevented. Moreover, it becomes possible to prevent the overrun of the cell of a rapid temperature rise, and comparatively rapid breakage can be prevented, without bringing about lowering of the capacity consistency by adding an additive to the interior of an electrode. Therefore, the effect to the energy density of a cell is small, and effectiveness has enough in high capacity-ization of a cell.

[0033] as mentioned above, the thing for which the fill of an electrode active material is reduced by using a carbon material with a large specific surface area which carried out gas adsorption to the electric conduction assistant -- there is nothing -- high capacity -- it is -- high -- a safe lithium secondary battery can be offered and industrial and commercial value is size.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the outline block diagram of the nonaqueous electrolyte rechargeable battery of this invention.

[Description of Notations]

1 [-- A negative electrode, 5 / -- A separator, 6 / -- An insulator, 7 / -- A cell can, 8 / -- A cell lid, 9 / -- A gasket, 10 / -- A positive electrode, a negative-electrode terminal, 11 / -- The component for current cutoff 12 / -- Center pin.] -- A positive-electrode charge collector, 2 -- A positive electrode, 3 -- A negative-electrode charge collector, 4
